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Waxes

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66.1 Introduction

A discussion on the use of waxes for coatings must begin with an explanation of what constitutes a wax. Because of the diverse nature of products included in the class of waxes, this is not a simple objective.

There are few references that discuss waxes and their applications. In 1956 A.H. Warth published a book that covered the types and applications of waxes available.[1] More recent general references on wax are a two-volume work entitled *Industrial Waxes* by H. Bennett[2] and *Wax: An Introduction* by R. Sayers.[3] The Chemical Specialties Manufacturers Association (CSMA) has also published a booklet entitled *Technology of Waxes*, which contains several articles dealing with the chemistry and physical properties of waxes of various types.[4]

These are the major sources for information on waxes. Numerous articles are available, which may discuss one specific type of wax or cover an application area, often only casually mentioning wax usage.

66.2 Definition

In the medieval days (and earlier) the definition of waxes was very simple. Wax was the substance produced by bees that prevented the honey from running out the bottom of the hive. Beeswax was the only wax known. In 1848 Justus Liebig characterized beeswax as consisting predominantly of long chain fatty acids, esters, and alcohols. Several other natural waxlike products from plant and animal sources had a similar chemical makeup. The definition of a wax was still fairly vague. If the chain length of a substance was longer than the C_{16} to C_{18} associated with fatty acids, in a chemical sense, it was a wax.

In the 20th century, a large number of new products were introduced. Some of these were waxlike but did not conform to the chemical definition. People wanting wax defined by physical properties won out over those supporting a chemical definition. Therefore, products that have waxlike properties but are not based on long chain esters (e.g., paraffins and low molecular weight polyethylenes) are referred to today as waxes.

In 1954 the Deutsche Gesellschaft für Fettwissenschaft (DGF) established a wax definition based on physical properties and abandoned the efforts to maintain the chemical definition. A revised version was published in "DGF—Einheitsmethoden Abteilung M—Wachse" in 1975 (Table 66.1). The failure to put

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TABLE 66.1 Definition of Wax[a] from a German Technical Society

1.	20°C (68°F) kneadable solid to brittle hard
2.	Macro to microcrystalline, translucent to opaque but not glasslike
3.	Melting above 40°C (104°F) without decomposition
4.	Relatively low viscosity slightly above the melting point
5.	Consistency and solubility are strongly dependent on temperature
6.	Capable of being polished (i.e., buffable) under slight pressure

[a] The term "wax" is a collective name for a number of natural or synthetic substances. If, in borderline cases, more than one of these properties cannot be met by a substance, it does not represent a wax in the actual meaning of this definition.

Source: Einheitsmethoden, Abteilung M—Wachse, proposed in 1954 and revised in 1975 by the Deutsche Gesellschaft für Fettswissenschaft.

specific limits on most of the listed properties (e.g., no upper limit on melting property and no specific viscosity range) demonstrates the diverse properties of waxes. Only five of the six DGF properties must be met for a product to fall under the definition of wax.

66.3 Types

One generally attempts to classify waxes into one of the three basic categories of animal, vegetable, or mineral, but even this approach encounters difficulties. Mineral waxes are in reality primordial vegetation deposits subjected to pressure and millions of years of aging to form oil and coal (i.e., aged vegetable wax). A fourth classification is also needed for the numerous synthetic waxes that are derived from the three main sources. The question also arises as to how much refining and alteration of a wax can be made before it is no longer considered a natural wax but a synthetic wax.

66.3.1 Animal Waxes

Animal waxes are derived from two separate sources. One source is by-products produced by the animal (beeswax). The second source is from the animal itself (fatty acid derivatives).

Lesser known waxes include Chinese and shellac waxes obtained from secretions of various insects and wool wax refined from lanolin (extracted from sheep's wool). Commercially, they are found only in a few specialized areas.

66.3.1.1 Fatty Acids

Fatty acids and their derivatives come from processing tallow and lard. These products are produced in very large volume. The production is often considered to be an industry in and of itself, and these materials are not always thought of as wax products. Chemically they consist of C_{16} and C_{18} esters of glycerine. Typical products are stearic acid, glycerol tristearates, and glycerol monostearates.

66.3.1.2 Beeswax

Beeswax is the oldest known wax. It consists of long chain fatty acids and long chain monovalent alcohols. The exact composition of beeswax is extremely complex, and even today an exact duplicate based on synthetic materials has not been accomplished.

66.3.2 Vegetable Sources

Vegetable waxes are obtained from the leaves, stems, or berries of plants. These waxes consist mainly of alkyl esters. Chain length and type vary considerably depending on the surface.

66.3.2.1 Leaf Waxes

Leaf waxes are obtained by extracting wax from the leaves. They are also referred to as palm waxes.

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The leaf wax of greatest commercial significance, carnauba wax consists mainly of esters of alkyl alcohols (C_{24} to C_{34}) and alkyl acids (C_{18} to C_{30}). There are also substantial amounts of diesters and hydroxy esters. These hydroxy esters are believed to provide some of the unique paste forming properties and the ability to form microemulsions associated with carnauba wax.

Carnauba wax is extracted from the leaves of the carnauba palm (*Copernica cerifera*), which grows in the north and northeast regions of Brazil. The tree is also grown in other regions (Sri Lanka, West Central Africa), but only in Brazil are weather conditions suitable (torrential rains followed by a hot, dry windy period) to form significant wax deposits on the leaves.

66.3.2.2 Stem Waxes

Stem waxes include flax wax, sugarcane wax, and bark wax (Douglas fir). Efforts to develop these waxes commercially have met with limited success.

66.3.2.3 Berry or Fruit Waxes

A large number of waxlike products are derived from the fruit of various plants. Some waxes exist in the natural state as an outer coating on the fruit (bayberry and Japan waxes). Another source is refined and modified vegetable oils (i.e., hydrogenation). The cocoa fatty acid groups (C_{12} to C_{14}) represent the largest segment, but these are marginally included in the category of waxes because most derivatives are soft and low melting.

Castor wax is derived from castor oil, which is obtained from the seeds of *Ricinus communis*, a plant that grows in most tropical regions. Castor oil is predominantly (90%) the triglyceride of 12-hydroxystearic acid, with a double bond in the 9–10 position. Hydrogenation of the double bond forms the castor wax.

66.3.3 Mineral Waxes

Mineral waxes are obtained from oil and coal deposits. The name "mineral wax" has nothing to do with the composition but derives from the source (which is beneath the earth's surface). They are sometimes referred to as "earth waxes."

66.3.3.1 Paraffins

Paraffins are extracted from oil. The amount and type of wax present depends on the source of the oil. The paraffin is normally separated from the oil, distilled into several fractions, and sold as commodity items by the oil refineries.

66.3.3.2 Microcrystalline Waxes

Microcrystalline waxes are normally the higher molecular weight fractions from the paraffin extractions. They vary in hardness and melt properties depending on molecular weight distribution and branching. The name "microcrystalline" evolved from the discovery that these higher melting paraffins were not amorphous but consisted, to a high degree, of microcrystalline structures.

66.3.3.3 Montan Waxes

Montan waxes are extracted from soft coal deposits located predominantly in Germany, where the wax content in certain coal deposits is 10 to 15%. The coal is crushed and extracted with solvents to yield a dark brown to black crude montan wax with a wax content of 50 to 60%.

66.3.4 Synthetic Waxes

66.3.4.1 Polyethylene and Polypropylene Waxes

Polyethylene waxes are made by polymerization of ethylene to form ethylene chains similar to polyethylene resin but much lower in molecular weight (2000 to 10,000). The waxes can be oxidized by a variety of methods to produce waxes that are emulsifiable.

Polypropylene waxes are formed by controlled polymerization of propylene.

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66.3.4.2 Modified Montan Waxes

Modified montan waxes are derived from coal. The crude montan waxes are subjected to a series of solvent extractions and oxidized with chromium trioxide (CrO_3) generically referred to as the Gersthofen process. The CrO_3 selectively attacks tertiary carbon structures, leaving behind only the linear montanic esters and acids. After oxidation has been completed, a light-colored product consisting mainly of montanic acid is formed. The montanic acids can be reesterified with various alcohols and polyols and partially saponified to give a series of montan ester wax products having various properties.

66.3.4.3 Miscellaneous Synthetic Waxes

Fischer-Tropsch waxes are made by reacting carbon monoxide (from the coal gasification process) with hydrogen gas to form a hydrocarbon wax.

Polyglycol waxes are high molecular weight chains of ethylene oxide that form a wax-like product.

Oxidized hydrocarbons (paraffins, microcystalline, and polyethelyene waxes) are formed by oxidation (generally air blown) of hydrocarbon waxes to form a large variety of emulsifiable waxes.

66.4 Coating Applications

Various waxes are used in different application areas for coatings to enhance certain physical properties.

66.4.1 Mechanism

Waxes generally function by one of two basic mechanisms:

The "ball bearing" mechanism is a dispersion of discrete wax particles throughout the coating matrix. The particles that protrude above the film surface prevent the abrading media from contacting the coating surface. Instead, the other surface glides over the protruding wax particles, causing little damage to the surface.

The "migration" mechanism involves migration of the wax to the film surface, where it aids in formation of a smooth glossy film. In some applications, the plastic nature of the wax aids in filling voids formed as the solvent evaporates or the specific volume changes during curing of the resinous components.

66.4.2 Property Enhancement

The major properties affected by waxes are surface related.

66.4.2.1 Gloss

A high gloss is obtained from waxes predominantly by the migration mechanism. The waxes tend to fill the microvoids formed as the coating dries to provide a smooth continuous film. Often only small amounts of waxes are needed (0.5 to 2% of solids) to obtain a gloss improvement. In fact, too much wax can lead to formation of wax solid on the surface, resulting in a dull haze. A high gloss can be obtained by buffing the surface (property 6 in Table 66.1), but this is not practical in most situations. If the excess wax were to continue to migrate, the haze could return after several days (or weeks).

66.4.2.2 Matting

A matte (flat) surface is the opposite of high gloss, but both effects can be obtained using waxes. To obtain a matting effect, the type of wax and method of incorporation must be chosen to maximize the "ball bearing" mechanism. The wax particles that protrude above the surface diffuse the light to reduce glare. Particle size is very critical in obtaining a smooth, silky matte finish that does not feel rough or look dull or hazy. Dispersibility in the paint or varnish vehicle is important to obtain a uniform surface.

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Silicas are often used as matting agents, but their high density can lead to problems with settling out. Combinations of waxes and silica can lead to optimum effects. Using agents with differences in refractive indexes can further enhance matting effects without forming a haze.

66.4.2.3 Slip

Waxes can reduce the coefficient of friction by aiding in the formation of a smooth surface, as discussed in Section 66.4.2.1, or by reducing the number of contact points by gliding over the wax particles (ball bearing mechanism) discussed in Section 66.4.1.

Soft oily-type agents (soft, microcrystalline waxes or silicones) can also be used to form a slippery lubricating film on the surface. Mar resistance and blocking generally are very poor with this approach.

66.4.2.4 Abrasion Resistance

The ability of waxes to improve abrasion resistance is generally related to their ability to increase slip.

66.4.2.5 Antiblocking

Blocking can be reduced by incorporating hard wax particles (ball bearing mechanism) to reduce surface contact. A compromise in gloss must often be accepted. Some hard waxes can reduce blocking by absorbing oils and reducing the migration to the surface of other soft tacky components present in the coating formulation.

66.4.2.6 Antisettling/Antisagging Agents

When dissolved and cooled in solvent-based systems, many waxes form a thixotropic dispersion. The formation of a gel, which will liquify when stirred, will reduce the tendency of denser materials (pigments, fillers, etc.) to settle out.

66.4.3 Incorporation Methods

How a wax is incorporated into a coating formulation can affect the end performance. Particle size and uniformity of dispersion are critical factors. The best method depends on the type of wax and the desired end effect. Four basic methods are used.

66.4.3.1 Wax Compounds

Solvent-dispersed pastes are formed by heating the wax in a suitable solvent (ideally the same as the vehicle used in the coating formulation) and quickly cooling to room temperature under high shear conditions. The rapid cooling and high shear rates are required to prevent the formation of large seed crystals, which would appear as blemishes in the coating when applied.

Minor variations in the production of wax compounds can cause changes in the particle size distribution. Because of the sensitivity related to production conditions of wax compounds, most users rely on wax compound producers instead of preparing such waxes in-house.

66.4.3.2 Micronized Powders

Air milling and classifying the wax powder gives the optimum control of particle size. Micronized powders are based mainly on very hard, high melting waxes such as polyethylene waxes, amides, and polytetrafluoroethylene (PTFE). According to the wax definition, PTFE is not a wax, but because it is used in the same area associated with waxes, it is often included in discussions on wax applications, Attempts to prepare these waxes in a compound form is difficult. Their crystallinity invariably leads to formation of larger particles if the procedure is not properly done.

The dry powder reduces the handling of flammable and hazardous solvents often associated with waxy compounds. Both solvent- and water-dispersible grades are available. On the negative side, improper handling can lead to dusty conditions and explosion hazards. Micronized powders are also more expensive on a per-pound basis (however, greater efficiency can lead to lower use levels).

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66.4.3.3 Milling

The wax can be obtained as a coarse powder and milled in the same manner as pigments, or along with the pigments. This approach provides the end user with wax at the lowest cost. However, the time involved and the cost of the equipment rarely justify the savings in raw materials. Those who currently use this approach do so because they already have the equipment, which would be idle otherwise.

66.4.3.4 Emulsification

This approach is limited to water-based systems. The emulsion can be prepared in-house, provided the equipment is available, or it can be supplied by outside producers. The wax must be an emulsifiable type. Most commonly used for emulsification are oxidized polyethylene waxes and the refined montan waxes.

References

1. A. H. Warth, *Chemistry and Technology of Waxes,* 2nd ed. New York: Reinhold, 1956.
2. H. Bennett, *Industrial Waxes: Vol. I, Natural and Synthetic Waxes; Vol. II, Compounded Waxes and Technology.* New York: Chemical Publishing Co., 1975.
3. R. Sayers, *Wax: An Introduction*. London: European Wax Federation and Gentry Books Limited, 1983.
4. "Wax technology," extracted from *Proc. Chem. Spec. Manuf. Assoc. 61st Mid-year*, pp. 86–111 (1975).

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